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Project Title: Global Atmospheric Measurements Experiment on Tropospheric Aerosols and Gases (GAMETAG)

Project No: G-35-632 (Includes sub-project B-481/EES)

Project Director: Dr. Douglas D. Davis

Sponsor: National Science Foundation, Washington, D.C. 20550

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_ Final Fiscal Report
_ Final Report of Inventions
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_ Other _____

Assigned to: Geophysical Sciences (School/[redacted])

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CA–4 (1/79)

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT

NSF FORM 98A

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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology School of Geophysical Sciences Atlanta, Georgia 30332	Atmospheric Sciences	ATM 76-81487
	4. Award Period From 1/77 To 1/79	5. Cumulative Award Amount $600,400

6. Project Title

Global Atmospheric Measurements Experiment on Tropospheric Aerosols and Gases (GAMETAG)

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

Phase I of Project GAMETAG was designed around four basic objectives: (a) demonstrate the overall operational feasibility of a sophisticated global aircraft sampling program; (b) provide new information on the importance of hydroxyl radical reactions to the overall definition of tropospheric chemistry; (c) provide an initial data base upon which global tropospheric budget assessments could be carried out for halocarbons, ozone, sulfur, carbon, and nitrogen species; and (d) provide limited but yet significant new information on the global distributions and characteristics of tropospheric aerosol species. Representing a joint scientific venture between scientists from several universities, private industry, and government labs, the GAMETAG project successfully carried out two major flight operations during the years 1977 and 1978. Using an L-188C turbo Electra, owned and operated by the National Center for Atmospheric Research, a global latitude range of 70°N to 57°S was traversed, involving over 250 hours of sampling time. During these flight operations, measurements were performed both in the free troposphere and in the atmospheric boundary layer.

In addition to the measurements of meteorological variables such as temperature, pressure, vertical and horizontal wind speeds, dew point, IR ground emissions, and the UV flux, concentration data were recorded on over twenty trace gases. They include: O_3, OH, H_2O, CO, CO_2, CH_4, N_2O, HNO_3, NO (upper limit only), SO_2, COS, F-11, F-12, CCl_4, CH_3CCl_3, CH_3Cl, CH_3I, C_2H_6, C_2H_4, and C_6H_6. Also measured during the project were the following aerosol parameters: size/number distribution, the imaginary index of refraction, and the mass concentration of the species NH_4^+, SO_4^-, NO_3^-, and Cl^-.

Preliminary analyses of the above data were reported on at the 1978 Fall AGU meeting in San Francisco, California. Expanded data sets, together with more extensive interpretative analyses of the GAMETAG results are to appear in a special issue of the Journal of Geophysical Research in mid 1980.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses				✓	July 1980
b. Publication Citations				✓	July 1980
c. Data on Scientific Collaborators		✓			
d. Information on Inventions	✓				
e. Technical Description of Project and Results		✓			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Dr. Douglas D. Davis		Nov. 20, 1979

NSF Form 98A (5-78) Supersedes All Previous Editions

Form Approved OMB No. 30R0101

Final Report on

NSF Grant #ATM7681487

GAMETAG 1977 & 1978

Prepared By:

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A. 1977 Flight Operation

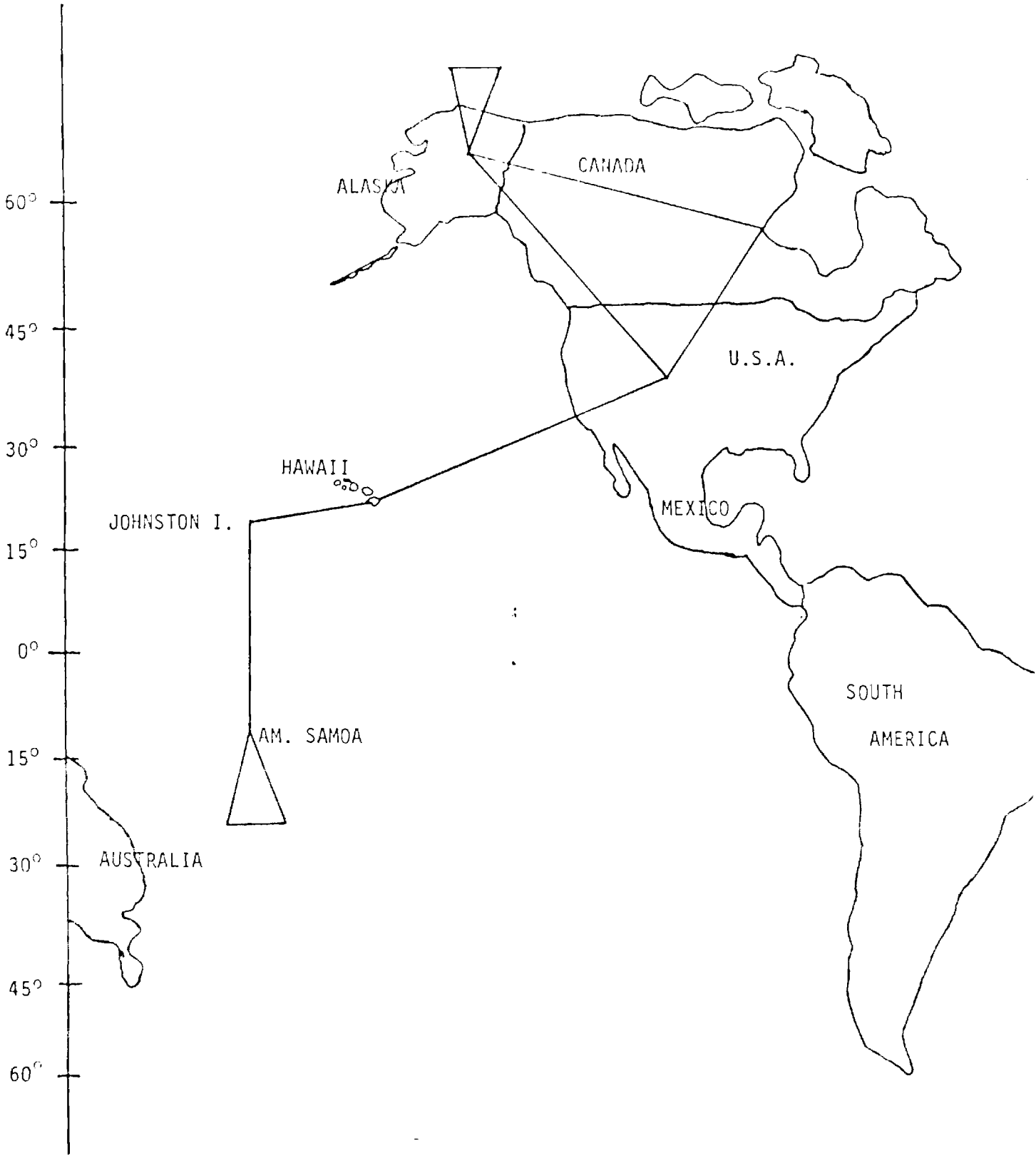
1. General Summary - During the summer of 1977, two GAMETAG flight operations were carried out involving 110 hours of flight time. These flights covered the latitude range of 70° N to 25° S. The sampling profile consisted of a stair step configuration which alternated between boundary layer air and the free troposphere, (see sampling profile displayed in Fig. 1).

Although complete data analyses on the 1977 flight series are not yet complete, several major findings are already quite apparent. These findings are related to the atmospheric species: OH, O_3, CO, COS, SO_2, HNO_3, HCl, CH_3CCl_3, CH_3Cl, low molecular weight hydrocarbons and aerosol species. A summary statement on each of these species is provided in the following text.

OH (Hydroxyl Free Radical): PI; Dr. D. D. Davis

Approximately thirty-five hours of OH data was collected during the 1977 summer GAMETAG program. The data processing to date has been confined primarily to the South Pacific where measured OH concentration values were found to be strongly dependent upon whether the sampling occurred in the marine bundary layer or above it. Over the latitude range of 20° S to 20° N, for example, it was observed that the OH concentration frequently changed by one order of magnitude in passing from one atmospheric zone to another. Typical results for boundary layer air versus the free troposphere (up to altitudes of 6 km) were 1.5×10^7 and 1.5×10^6 molecules/cm^3, respectively. The above values reflect measurements recorded during the solar flux window of 11:00 A.M. to 2:00 P.M. One major exception to the typical values of OH noted above were those

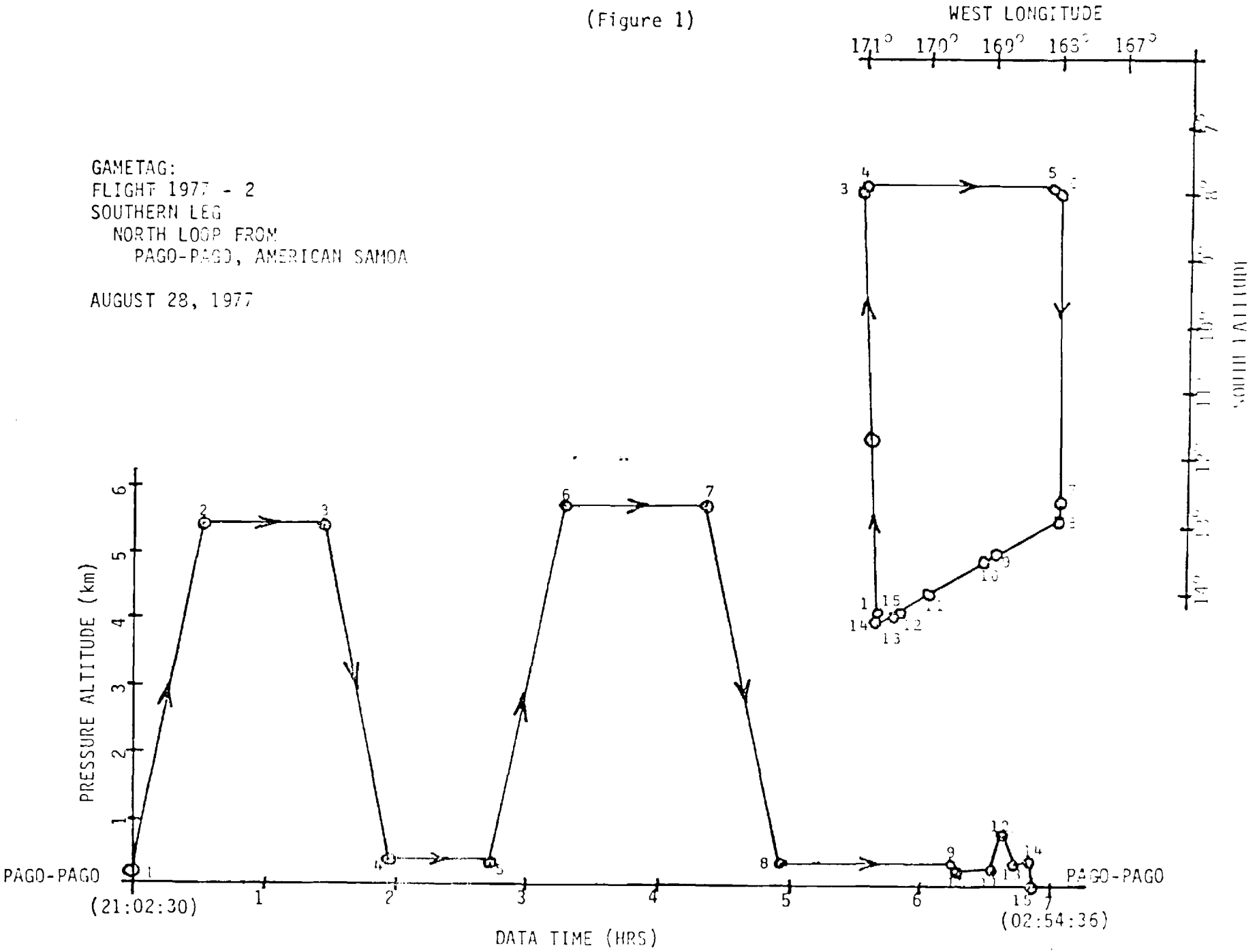
1977 SUMMER GAMETAG FLIGHT OPERATION



(Figure 1)

GAMETAG:
FLIGHT 1977 - 2
SOUTHERN LEG
NORTH LOOP FROM
PAGO-PAGO, AMERICAN SAMOA

AUGUST 28, 1977



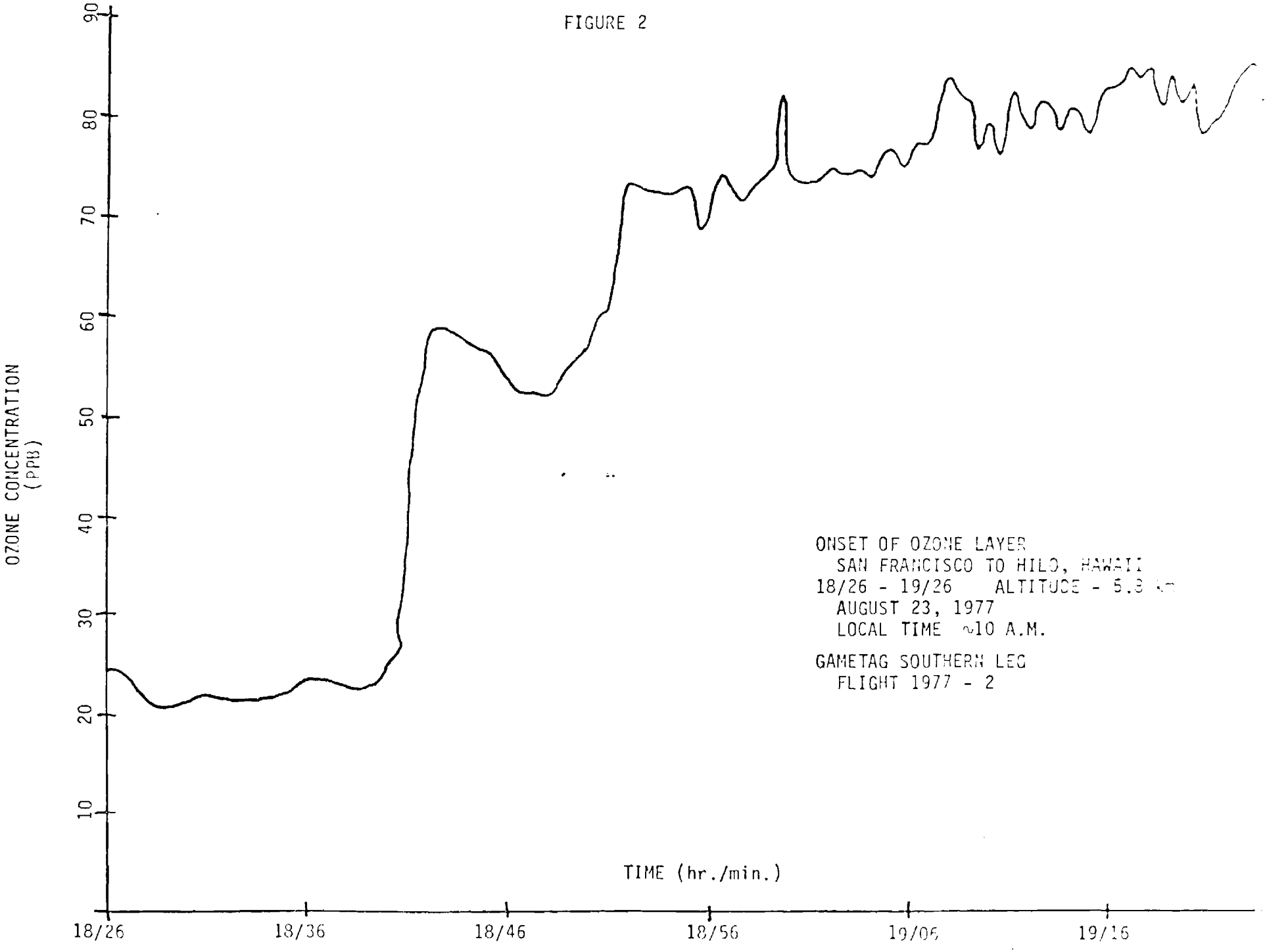
measurements taken in the ITC Zone, which during our flight operation occurred between approximately 11° and 7° N latitude. In this tropical region, where storms are abundant, the high altitude (6 km) values of OH were two to three times greater than those observed outside the ITC Zone for the same altitude and solar flux.

From simple zero-D photochemical modelling calculations (using direct measurements of H_2O, O_3, CO, CH_4, UV Flux and Temperature), it has been shown that the single major factor controlling the above-cited concentration changes in OH was the strong gradient in water vapor with altitude. An additional factor which also appeared to be of considerable importance in defining the OH gradient were the changes observed in the concentration levels of O_3. The NO gradient would also be expected to have some impact on the variability of OH with altitude; however, at this time, the NO data collected have resulted in only an upper limit on the concentration of this species of 150 pptv.

O_3 (Ozone): PI's: Mr. Art Wartburg, Dr. E. Danielsen, and Dr. D. D. Davis

Certainly one of the major surprises of the South Pacific GAMETAG flight was the observation that marine boundary layer air and middle tropospheric air over large regions of the Pacific Ocean can differ enormously in thier respective ozone levels. During our sampling flights, marine boundary layer air (average depth ~1.3 km) over the latitude range of 37° to 12° N and 10° to 25° S was typically found to contain average levels of ozone of 17 ppb with minimums of 8 and highs of 25 ppb. In sharp contrast to this, above the boundary layer, up to ~6 km, average ozone layers ran 35-40 ppb. Equally important was the observation that superimposed on this higher average level of ozone were intense ozone layers (typically .3 to .6 km in thickness) with maximum concentrations

FIGURE 2


OZONE CONCENTRATION (PPB)
90
80
70
60
50
40
30
20
10
TIME (hr./min.)
18/26
18/36
18/46
18/56
19/06
19/16
ONSET OF OZONE LAYER
SAN FRANCISCO TO HILO, HAWAII
18/26 - 19/26 ALTITUDE - 5.3 KM
AUGUST 23, 1977
LOCAL TIME ~10 A.M.
GAMETAG SOUTHERN LEG
FLIGHT 1977 - 2

of ozone reaching ~90 ppb, (see Figure 2). In many cases when major altitude changes were carried out between the boundary layer and 6 km, three to five ozone layers could be observed superimposed on a broad continuous background level of ozone. These tropospheric Pacific ozone layers (TPO layers) were observed over thousands of miles of Pacific Ocean. Only upon reaching the intertropical convergence zone near the equator, 12° N latitude, was there a marked decrease in the average level of ozone above the boundary layer and in the number and intensity of TPO layers. Upon reaching southern latitudes of ~16° S, we once again encountered significant ozone layering. Simultaneous measurements of several other atmospheric species strongly suggest that the origin of the observed ozone layers was indeed the lower stratosphere. If this phenomenon occurs with some regularity, it will most certainly have a major impact on tropospheric ozone budget calculations as well as overall tropospheric chemical modelling.

CO (Carbon Monoxide): PI's; Mr. L. Heidt, and Dr. R. Rasmussen

Previous global measurements of CO reported by Seiler (1974) have indicated that a substantial concentration gradient (nearly a factor of four or five) exists for this trace gas between the northern and southern hemispheres. In contrast to Seiler's data, results from the summer 1977 GAMETAG flight indicate the CO concentration gradient to be between a factor of 1.3 and 2.0. Whether the smaller CO gradient observed by GAMETAG scientists reflects a seasonal variation or a difference in the Pacific Ocean versus the Atlantic Ocean, (the principal source of Seiler's data) is not known with certainty at this time. However, since the tropospheric CO budget is of major importance to tropospheric chemical models, the resolution of this question must be considered of very high priority (see new results under 1978 flight operation).

COS (Carbonyl Sulfide): PI; Dr. Alan Bandy

Previous to the recording of the 1977 summer GAMETAG data base on COS, little if anything was known about the global distribution of this compound.

The general trend observed during the GAMETAG flights was that of seeing lower values both to the north and south of $\sim 40^{\circ}$ N latitude (the value at 40° N being $\sim$400 ppt).

SO_2 (Sulfur Dioxide): PI; Dr. Alan Bandy

SO_2 data from the South Pacific (the first ever) showed the average value for this species to be $\sim$200 pptv. Further improvements in the calibration procedure for the real time SO_2 analyzer should permit both altitude and latitude gradients in SO_2 to be more clearly defined.

HNO_3 (Nitric Acid): PI; Dr. Berry Huebert, and Dr. Al Lazrus

As was the case for several other trace gases, the HNO_3 data collected during the 1977 GAMETAG flight operation represents the first of its kind for the natural troposphere. These results can be summarized as follows: (a) The HNO_3 concentration over populated areas was typically found to be ten times higher (in boundary layer air) than over remote areas of the Pacific Ocean or Northern Canada. Above the boundary layer this difference was much more variable, ranging from a high of ten to a low of two; (b) HNO_3 levels both above and within the atmospheric boundary layer were found to be nearly the same (<.02 to .20 ppbv) over remote continental or marine areas; and (c) For those regions uninfluenced by anthropogenic emissions (Northern Canada and the South Pacific), it appears that HNO_3 together with HCl may be two of the major components which control the acidity of rain.

HCl (Hydrogen Chloride) or Acidic Chlorine Species: PI; Dr. Berry Huebert, and Dr. Al Lazrus

(a) Although most of the remote HCl concentrations both above and within the boundary layer were in the range of less than 0.1 to 0.7 ppbv, seven values were between 1 and 2 ppbv. Of these high values, six were above the boundary layer. There is no evidence of a strong negative HCl gradient with altitude; (b) HCl near populated areas ranged from 0.4 to 2 ppbv, and was generally higher than most remote values; (c) there is some evidence suggesting that heterogeneous chemistry produces HCl in the marine boundary layer; (d) the presence of liquid water, either as clouds or precipitation, can dramatically effect HCl levels.

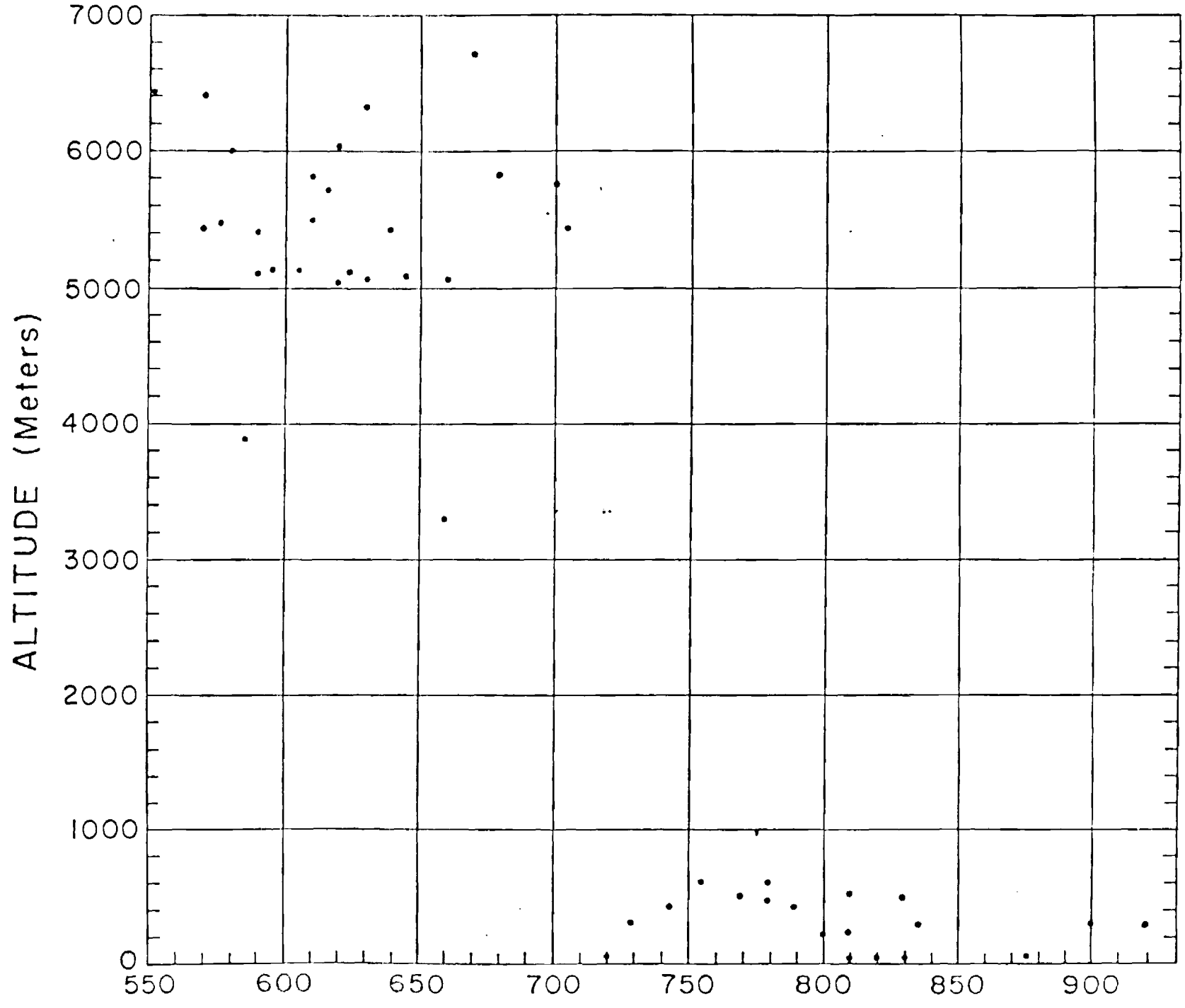
CH_3CCl_3 (Methyl Chloroform): PI's; Mr. Leroy Heidt and Dr. R. Rasmussen

In contrast to previous measurements of the global distribution of methyl chloroform, the northern-southern hemispheric gradient observed during the 1977 GAMETAG flight was a factor of 1.1 to 1.4. Earlier studies have resulted in reported gradient factors of 1.9 to 2.0. We believe that the latest GAMETAG results do raise a serious question about the validity of using global methyl chloroform measurements as a means of computing global average concentrations for the hydroxyl radical.

CH_3Cl (Methyl Chloride): PI; Dr. R. Rasmussen

Methyl Chloride is now believed to be one of the major natural sources of gaseous atmospheric chlorine. Its source has been thought to be marine waters where the exchange reaction between Cl^- and iodine in the form of CH_3I could produce directly the compound CH_3Cl. Until now, however, little direct evidence existed which demonstrated the importance of the marine source. As shown in Figure 3, GAMETAG data collected both in and above the marine boundary layer shows very convincingly a concen-

CH_3CL DATA FIG. 3



tration gradient of ∿1.4 (the marine boundary layer typically extended up to an altitude of 1.3 km). The most direct explanation for this observed fall off at higher altitudes is that the ocean is, in fact, a major source of CH_3Cl.

Low Molecular Weight Hydrocarbons- C_2H_6, C_2H_2, and C_2H_4 : PI; Dr. Rasmussen

All samples collected in remote areas of Northern Canada and the South Pacific showed C_2 hydrocarbon levels to be approximately one ppbv or less. We believe the above finding is consistent with the observation that in no case was a high level of ozone (greater than ∿30 ppbv) found in boundary layer air over the aforementioned remote areas. The photo-chemical generation of ozone is believed to require both significant concentrations of hydrocarbons and nitrogen oxide.

Other Gases: F-11, F-12, CCl_4, N_2O, CH_4, and CO_2

Although extensive measurements were recorded for each of the above gases, as of this time no major surprises in the observed concentration levels for these species have been found.

UV Flux: PI, Dr. Bach Sellers

During the 1977 GAMETAG flight, UV Flux measurements were recorded continuously throughout the 110 hrs. of flight time. Of critical importance in these measurements was the 30 Å resolution with which the UV flux was measured in the ozone photosensitive region of 3200 to 2900 Å. Although the complete processing of the 1977 data is awaiting the setting up of a computer interface to handle the aircraft data tape, several segments of data from the 1977 flight were hand processed. The results from this hand processed data were then used to calculate real-time values of the photo-chemical rate constant, J_1, i.e.

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

A summary of the J_1 values (and the conditions under which the UV Flux was measured) for fourteen flight segments of the 1977 GAMETAG operation has been given below in the form of Tables 1 and 2 and Figures 3 and 4.

Table 1

Flight conditions for several UVS measurement periods on the August-September 1977 GAMETAG flights

Meas. No.	Date 1977	GMT range (hrs-min)	Lat. (deg N)	Long. (deg E)	Alt. (km)	θ_{sun} (deg)	Ozone* (atm-cm)	$R_{n:p}$†	R** (ground)
1	8 Aug.	2023-2036	49.1	-131.0	5.46	33.5	0.247	0.379	0.304
2	9 Aug.	2315-2326	68.1	-159.0	1.81	52.9	0.239	0.148	0.058
3	10 Aug.	0052-0105	62.9	-155.4	5.41	54.1	0.266	0.308 (av)	0.127
4	11 Aug.	2007-2015	61.5	-127.6	5.68	46.7	0.241	-	(0.09)
5	11 Aug.	2102-2112	61.8	-121.3	0.89	47.9	(0.277)	-	(0.05)
6	11 Aug.	2311-2324	60.9	-102.5	7.60	65.0	(0.320)	0.308 (av)	0.216
7	23 Aug.	1846-1859	35.2	-127.1	5.43	32.8	0.238	-	(0.05)
8	25 Aug.	2157-2205	18.2	-156.7	3.32	10.2	0.223	0.135	0.053
9	29 Aug.	0020-0036	-8.9	-168.0	5.77	26.2	0.202	0.162	0.008
10	31 Aug.	2310-2325	-25.5	-169.7	5.75	33.9	0.251	0.256 (av)	0.139
11	1 Sept.	0031-0044	-24.5	-172.4	0.43	36.9	(0.263)	0.068	0.006
12	1 Sept.	2213-2223	-3.2	-170.0	0.59	18.5	(0.216)	0.061	0.061
13	2 Sept.	0031-0044	7.3	-169.4	5.39	20.3	0.212	0.210 (av)	0.075
14	2 Sept.	0122-0130	11.2	-169.6	5.44	31.7	0.220	-	(0.05)

*Values in parentheses are less accurate because of the low altitude of the measurement.

†Measured pyranometer flux ratios, upward going to downward going radiation in the 300 to 400 nm region. Dashes indicate no data available, and (av) is an average for data showing significant variations.

**Derived from pyranometer data. Values in parentheses are estimates from UVS results where no pyranometer data are available. The R values are for 300 to 400 nm radiation, and include cloud effects.

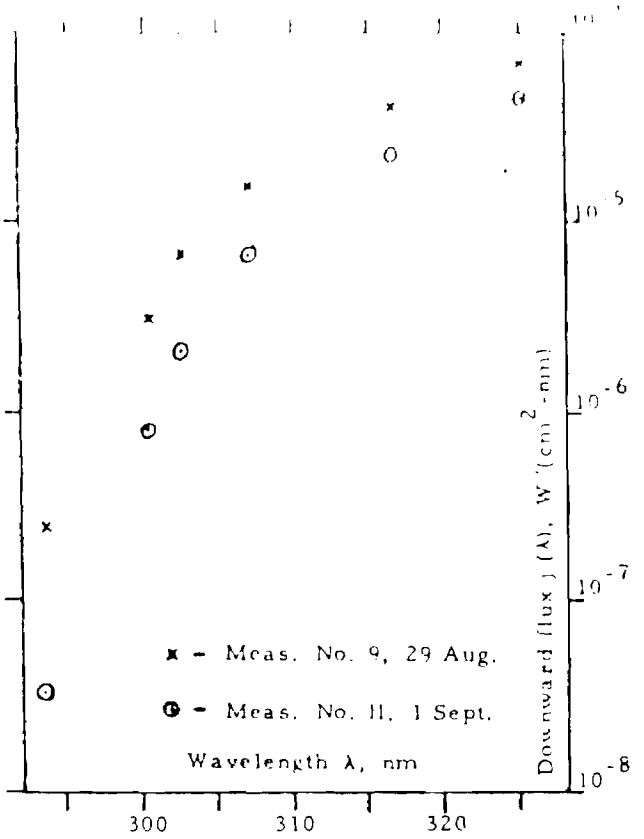


Figure 4 Two UVS measured downward fluxes for 290 to 330 nm.

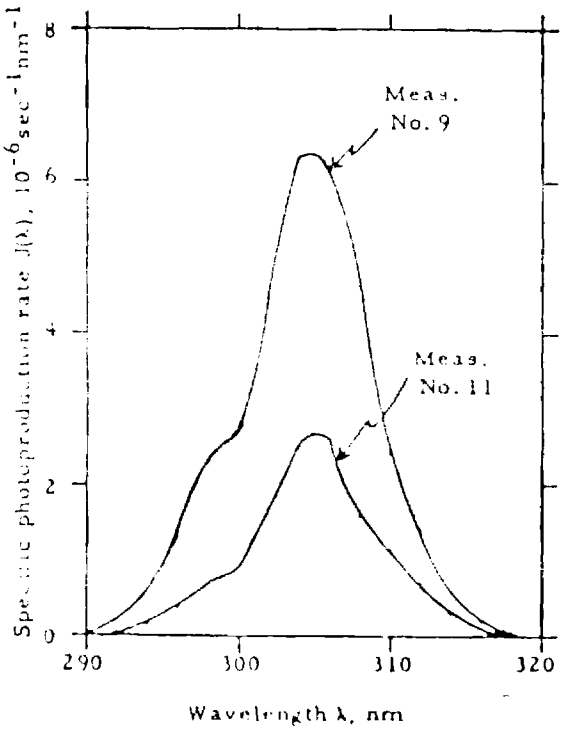


Figure 5. Plot of $O(^1D)$ specific photoproduction rate for fluxes of Figure 4.

Table 3

Rates of production of $O(^1D)$ from the photodissociation of O_3 for the August-September GAMETAG flights.

Measurement No. (Table 2)	$O(^1D)$ production rate constant, J_o (10^{-5}sec^{-1})*
1	5.78
2	1.74
3	2.04 (av)
4	(3.73)
5	(1.60)
6	0.63 (av)
7	(4.93)
8	5.66
9	6.70
10	4.76 (av)
11	2.66
12	4.54
13	6.07 (av)
14	5.63 (av)

*Values in parentheses use estimates for the ground albedo R. (av) indicates an average for data showing significant variations. See Table 2 footnotes.

Size-Number Distribution of Aerosols: P.I., Dr. Tony Delany

The 1977 GAMETAG data represents the most extensive data base ever collected on aerosol number distributions (in the size range from 0.125 μm to 15 μm) within and above the remote marine and continental boundary layer over the latitude range of 70° N to 25° S. Preliminary results from this flight can be summarized as follows: The variability on the size-number aerosol distribution was found to be strongly a function of the sampling location. In polluted areas (e.g. Imperial Valley, California), the total number of aerosol varied from 10^3 to 10^5 per cm^3. In strong contrast to those observations, in remote areas both within and above marine and continental boundary layers, the number density was in the range of 10^0 to 10^3 per cm^3. However, the number density was at the higher end of the range more often in the case of boundary layer air. A second finding from the 1977 flight was the observation of a bi-modal aerosol size distribution with mean radii in the range of 0.1 to 0.2 μm and .7 to 1.0 μm. This distribution was particularly characteristic of marine and continental boundary layer air. In a few cases, only the smaller size mode was observed in free tropospheric air over remote marine and continental areas.

Due to the extensive variability observed in the size-number aerosol distribution, a comprehensive data analysis will require input on aerosol chemical composition, optical properties, trace gas concentrations, and meteorological data. Thus, only after the completion of other GAMETAG analyses, will it be possible to carry out a more detailed interpretation of the aerosol size-number distribution.

Optical Properties of Aerosols: PI's, Dr. E.M. Patterson, Mr. Clyde Wyman and Dr. Gerald Grams

Most of the existing data on the optical properties of aerosols have been restricted to urban and continental areas. During the 1977

GAMETAG flights, extensive data on the optical properties of aerosols was collected over remote areas both within and above marine and continental boundary layer air. From a few select samples, a preliminary analysis has shown that there was very little variation in the complex index of refraction. Aerosols collected in free tropospheric air and in marine and continental boundary layer air all show values for the real index of refraction of $\sim$1.5 and values for the imaginary index of refraction of $\sim$0.01.

With input on the complex index of refraction and the size-number distribution, aerosol scattering coefficients are now being calculated using Mie theory. Later, these scattering coefficients will be compared with data collected on the polar nephelometer.

Chemical Composition of Aerosols: PI's, Dr. Barry Huebert and Al Lazrus

Fourty filter samples were collected during the 1977 GAMETAG flights. A summary of these results is here presented in the form of Table 3.

Table 3

location	$SO_4^=$ ppbm	NO_3^- ppbm	Cl^- ppbm	NH_4^+ ppbm
Within the marine boundary layer	$1.0<SO_4^=<3.0$ occasionally <1.0	$0.2<NO_3^-<1.1$	$1.9<Cl^-<16.5$	$0.01<NH_4^+<0.15$
Above the marine boundary layer	$0.1<SO_4^=<0.3$	0.2 or less	less than 0.3	less than 0.02 lowest NH_4^+ has been observed
Within the continental boundary layer, remote area	<1.0 lower than within marine boundary layer	0.2 or less	less than 0.3	less than 0.02
Near polluted area	1.7, 3.8, etc in general >1.0	$1.7<NO_3^-<3.5$	$0.5<Cl^-<0.9$	$0.14<NH_4^+<1.1$
Above the continental boundary layer, remote area	<1.0 in general higher than marine boundary layer	<0.3 data gives 0.48 due to intrusion of stratospheric air	<0.3 near storm or marine air intrusion reg $\sim$1.0	Average less than 0.02

The trends observed in the 1977 data are: (a) More $SO_4^=$ and NO_3^- were observed within the marine boundary layer (except near the polluted areas) which suggests that the ocean may be a source of both $SO_4^=$ and NO_3^-; (b) the Cl^- measurements are consistent with previously reported work; (c) there was a large variability on the NH_4^+ concentration. In all cases, more NH_4^+ was observed within the boundary layer than above the boundary layer. Over remote areas there was no major difference between continental and marine air.

2. Detailed Discussion of OH Results - During daylight hours, to a first approximation, processes (1)-(5) define the steady state photochemical equilibrium concentration for the hydroxyl radical, i.e.

$$(1)\quad O_3 + h\nu \xrightarrow{\lambda<3150\text{Å}} O(^1D) + O_2$$

$$(2)\quad O(^1D) + H_2O \longrightarrow OH + OH$$

$$(3)\quad O(^1D) + N_2 \longrightarrow O(^3P) + N_2$$

$$(4)\quad OH + CH_4 \longrightarrow CH_3 + H_2O$$

$$(5)\quad OH + CO \longrightarrow CO_2 + H$$

$$[OH]_{P.E.} = \frac{2k_2[H_2O][O(^1D)]}{k_4[CH_4] + k_5[CO]} \qquad \text{I}$$

or in terms of measurable parameters,

$$[OH]_{P.E.} = \frac{2k_2[H_2O]\dfrac{J_1[O_3]}{k_3[N_2] + k_2[H_2O]}}{k_4[CH_4] + k_5[CO]} \qquad \text{II}$$

Here, k_2, k_3, k_4, and k_5 are the temperature dependent gas kinetic rate constants for reactions (2),(3),(4), and (5), and J_1 is the photochemical rate constant for process (1).

OH concentrations estimated from equation II, however, must necessarily represent near minimum values for OH since both the interaction of the HO_x cycle with the NO_x cycle and the degradation of the CH_3 radical to CO are likely to result in an enhancement in the level of tropospheric OH. The effect of NO on the steady state OH concentration can be evaluated from an examination of the coupled set of reactions (5)-(8).

$$(5)\quad OH + CO \longrightarrow CO_2 + H$$

$$(6)\quad H + O_2 \xrightarrow{M} HO_2$$

$$(7)\quad HO_2 + NO \longrightarrow NO_2 + OH$$

$$(8)\quad HO_2 + HO_2 \xrightarrow{M} H_2O_2$$

In this case, depending on the NO concentration level, the competitive set of reactions (7) and (8) may or may not result in chain termination for HO_2 radicals. If, for example, reaction (7) were the dominant process, the OH radical would be recycled and reaction (5) would become a less efficient loss process for OH.

The CH_3 radical from reaction (4) can undergo extensive chemistry in converting to CO. Unfortunately, the kinetics of this degradation cycle are almost totally undocumented. The most practical approach to this problem is that of parameterizing the degradation scheme by assigning the four possible values for the generation of OH from each CH_3 radical.

Taking into consideration the impact of NO and CH_3 , a new expression for the steady state concentration of OH can be derived;

$$[OH] = \frac{J_1[O_3]}{k_3[N_2] + k_2[H_2O]} \times \frac{2k_2[H_2O]}{(A)k_5[CO] - (B)k_4[CH_4]} \qquad III$$

The term "B" in equation III is related to the degradation of the methyl radical and has been parameterized as:

$B = (x-1)$; where if

$x = 0$, $CH_3 \rightarrow 0$ OH

$x = 1$, $CH_3 \rightarrow 1$ OH

$x = 2$, $CH_3 \rightarrow 2$ OH

$x = 3$, $CH_3 \rightarrow 3$ OH

For moderately low levels of NO (<30 pptv), the quantity "A" can be reasonably well evaluated by expression IV,

$$A = \frac{(C)\, k_8[HO_2]}{k_8[HO_2] + k_7[NO]} \qquad IV$$

(Here the term "C" is the rain out efficiency or heterogeneous removal factor for hydrogen peroxide.) At yet higher levels of NO, the radical

termination step 9 also becomes important and more complex expressions than III and IV must be employed to evaluate the steady state OH concentration.

$$HO_2 + OH \rightarrow H_2O + O_2 \qquad (9)$$

Finally, at NO concentrations of one part-per-billion or higher, at least two other radical termination steps (10) and (11) must be included in the evaluations of the steady state concentration of OH.

$$OH + NO_2 \xrightarrow{M} HNO_3 \qquad (10)$$

$$HO_2 + NO_2 \xrightarrow{M} HOONO_2 \quad . \qquad (11)$$

In the text that follows, these authors have used equations III & IV to carry out zero-D OH modelling calculations using GAMETAG generated data for O_3, H_2O, CO, CH_4, and the UV flux (J_1). A comparison is subsequently made with in-situ measurements of OH which were carried out at the same location and time as those concentration measurements used in evaluating the [OH] from equation III. The three examples used in this comparison represent three extreme sets of conditions which were encountered over the latitude range of 20° S to 30° N.

In the comparison between theory and measurement which follows, it should be noted that with the exclusion of the terms "x" and |NO|, which are allowed to vary in the calculations, the probable error in the calculation of OH from eq. III is a factor of ±1.35. This error has been calculated from the uncertainties of the independent variables used in evaluating eqs. III & IV. The probable error in the measured value of OH has been calculated to be a factor of ±1.45. It is expected that both of these errors will become smaller in the future due to further refinements in our calibration techniques.

Comparison of Simple Photochemical Theory with OH

Measurements in Marine Boundary Layer Air

Measurements

Observation Time: 23:10 → 23:50 Z Temperature = 299° K

Local Time: ~12:30 P.M.

Altitude= .3 km

Latitude= 8° S

$[OH]_{Ave.}$ = 1.6 x 10^7/cm^3 *

$[H_2O]$= 21 Torr

$(UV)J_1$= 6.1 x 10^{-5}/s **

$[O_3]_{Ave.}$ = 18 ppbv (4.5 x 10^{11} molec/cm^3)

$[CO]_{Ave.}$ = 80 ppbv (2.0 x 10^{12} molec/cm^3)

$[CH_4]$= 1.6 ppmv (3.8 x 10^{13} molec/cm^3)

Calculations

Using eqs. III and IV, the above values for H_2O, O_3, CO, CH_4, and J_1, and gas kinetic rate constant values as:

k_2 = 2.3 x 10^{-10} cm /molec/s

k_3 = 5 x 10^{-11} cm /molec/s

k_4 = 7.0 x 10^{-15} cm /molec/s

k_5 = 2.9 x 10^{-13} cm /molec/s

k_7 = 8 x 10^{-12} cm /molec/s

k_8 = 3 x 10^{-12} cm /molec/s ,

the following OH steady state concentration values are calculated.

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* A typical integration time to obtain a 6/1 S/N was 6 minutes.

** J_1 calculated from UV Flux measurements (Panametrics, B. Sellers).

Case (I)

Very low concentration values assumed for NO, i.e. <5 pptv. Under these conditions the quantity "A" in eq. IV is equal to unity if "C" is set equal to one. For x = 0 then

$$[OH] = \frac{2(2.3 \times 10^{-10})[6.7 \times 10^{17}]\left[\frac{(6.15 \times 10^{-5})[4.5 \times 10^{11}]}{(5 \times 10^{-11})[2.0 \times 10^{19}] + (2.3 \times 10^{-10})[6.7 \times 10^{17}]}\right]}{(1)(2.9 \times 10^{-13})(2.0 \times 10^{12}) + (1)(7.0 \times 10^{-15})[3.8 \times 10^{13}]}$$

$$[OH] = .84 \times 10^{7}/cm^{3}$$

For x = 1

$$[OH] = 1.3 \times 10^{7}/cm^{3}$$

For x = 2

$$[OH] = 2.3 \times 10^{7}/cm^{3}$$

Case (II)

Let [NO] = 25 pptv

x = 0

c = 1

Then A = .5

Under these conditions, $[OH] = 1.3 \times 10^{7}$

For x = 1

$$[OH] = 2.4 \times 10^{7}$$

Although the 1977 flight did not permit an evaluation of the [NO] beyond an upper limit of 150 ppt, results from the 1978 GAMETAG flight indicate that South Pacific levels of NO are very likely to be <20 pptv. Thus, the real-time OH measurements would appear to be in good agreement with a range of values for "x" and the [NO] between Case I and Case II.

Comparison of Simple Photochemical Theory with OH Measurements in Marine Free Tropospheric Air

Measurements

Observation Time: 00:15 - 00:45 Z Temperature = 254° K

Local Time: ~ 1:30 P.M.

Altitude = 5.7 km

Latitude = 9° S

$[OH]_{Ave.}$ = 1.3 x 10^6/cm^3

$[H_2O]$ = .85 Torr

$(UV)J_1$ = 5.5 x 10^{-5}/s

$[O_3]$ = 36 ppbv (5 x 10^{11} molec/cm^3)

$[CO]$ = 80 ppbv (1.1 x 10^{12} molec/cm^3)

$[CH_4]$ = 1.6 ppmv (2.3 x 10^{13} molec/cm^3)

Case (I) - [All rate constants used in the calculations given below are the same as used in the boundary layer calculation except k_4 = 2.8 x 10^{-15}]

Very low levels of NO <5 pptv

C = 1

A = 1

Then for x = 0

$[OH]$ = 1.5 x 10^6/cm^3

for x = 1

$[OH]$ = 1.8 x 10^6/cm^3

for x = 2

$[OH]$ = 2.2 x 10^6/cm^3

Case (II)

NO level = 25 pptv

C = 1

Then A ≈ .5

For x = 0

$[OH] = 2.5 \times 10^6$

For x = 1

$[OH] = 3.5 \times 10^6$

From the above calculations it is seen that reasonably good agreement can be found between direct OH measurements and simple theory only for conditions involving low NO levels (i.e. <25 ppt).

Comparison of Simple Photochemical Theory with OH Measurements in the Intertropical Convergence Zone

Measurements

Time: 01:10 → 01:30 Z

Local Time: ∿ 2:30 P.M.

Temperature = 270° K

Latitude = 10° N

Altitude = 5.3 Km

$[OH]_{Ave.} = 3.1 \times 10^{6}/cm^{3}$

$[H_2O] = 2.7$ Torr (8.6×10^{16} molec/cm^{3})

$[CO] = 80$ ppbv (1.2×10^{12} molec/cm^{3})

$[O_3] = 18$ ppbv (2.7×10^{11} molec/cm^{3})

$[CH_4] = 1.7$ ppmv (2.6×10^{13} molec/cm)

$(UV)J_1 = 5.5 \times 10^{-5}/s$

Calculations

Case (I) - [All k values but k_4 are the same as in earlier calculations, $k_4 = 4.3 \times 10^{-15}$

Very low levels of NO assumed, i.e. <5 ppt.

"C" = 1

Then A = 1.0

Thus for x = 0

$[OH] = 1.7 \times 10^{6}/cm^{3}$

For x = 1

$[OH] = 2.2 \times 10^{6}/cm^{3}$

For x = 2

$[OH] = 3.2 \times 10^{6}/cm^{3}$

Case (II)

NO levels of ~25 pptv assumed

"C" = 1

Then A = .5

For x = 0

$[OH] = 2.7 \times 10^{6}/cm^3$

For x = 1

$[OH] = 4.3 \times 10^{6}/cm^3$

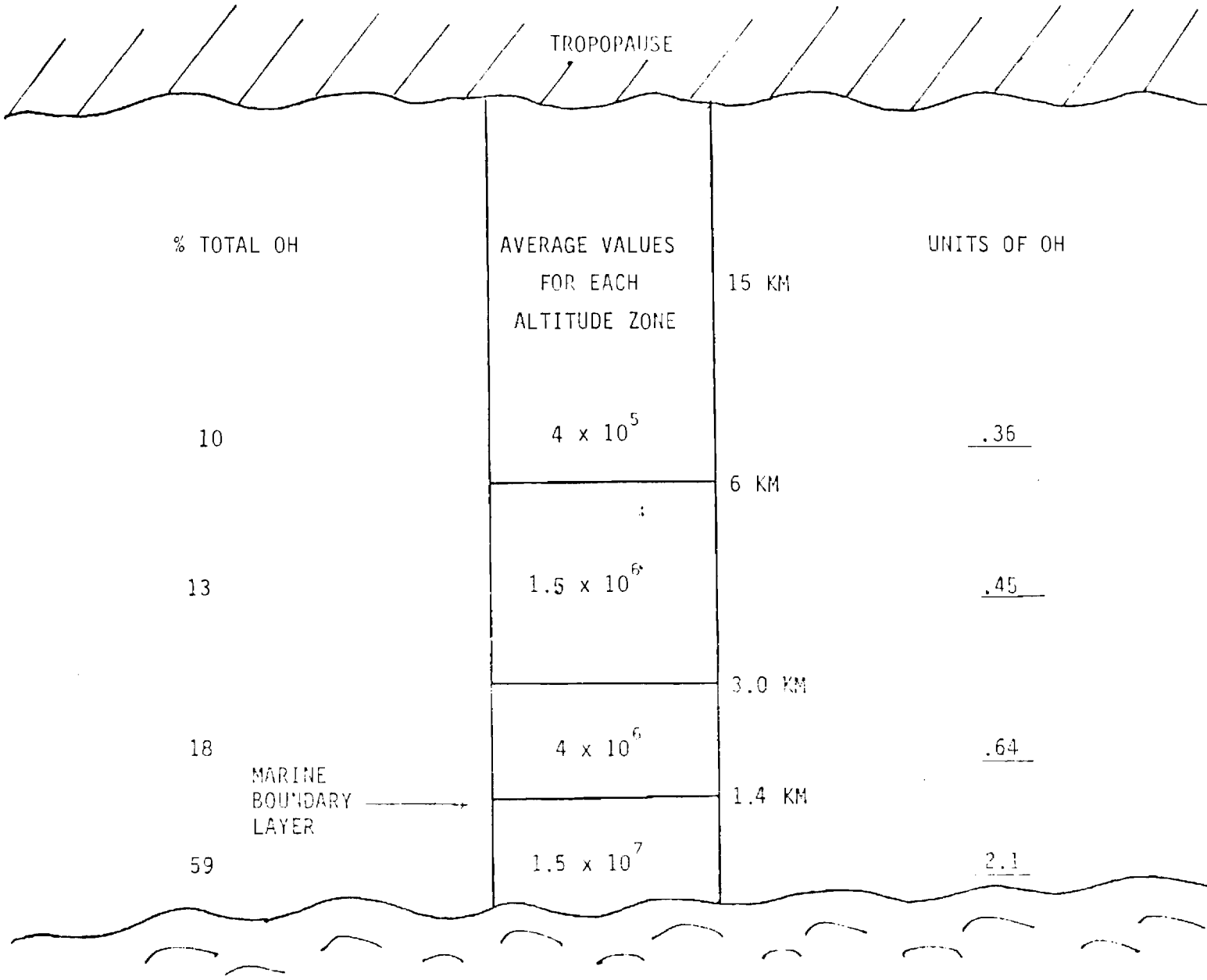
As indicated by both the O_3 and H_2O levels, the air sampled at 5.3 Km was well mixed with low altitude marine air. In this case, the in-situ measurements of OH are in good agreement with a range of conditions between Case I and Case II.

If typical OH measurements from the South Pacific are used in a simple box model of the troposphere, a first approximation can be made as to the relative importance of OH as a function of altitude. This is shown in diagram form in Fig. 6. In this figure, OH values up to 6 Km represent measured values; whereas, those above 6 Km have been estimated from model calculations. It is observed from Fig. 6 that approximately 60% of the OH in tropical latitudes could reside in the marine boundary. It is expected that this strong gradient in OH would have a very pronounced effect on both OH global budget calculations as well as calculations of the chemical lifetimes of numerous tropospheric trace gases.

FIGURE 6

RELATIVE IMPORTANCE OF OH

AS A FUNCTION OF ALTITUDE



B. 1978 Flight Operation (Prepared by D. D. Davis)

1. General Summary -

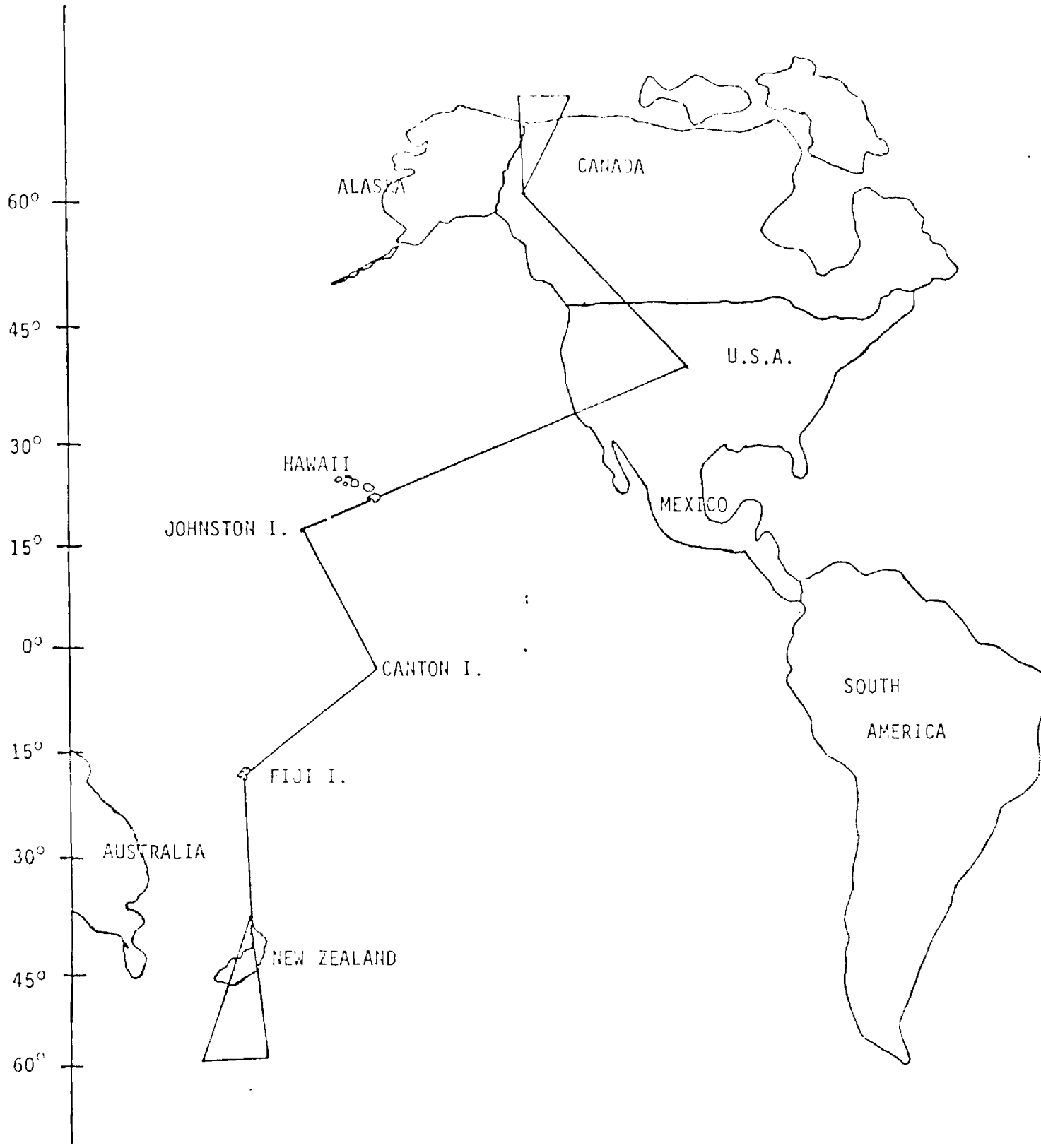
The 1978 Spring field sampling program involved two flight operations which used the NCAR turbo-prop Electra as the sampling platform. During this program ~125 hours of flying time were logged in, permitting a total latitude range of 70° N to 57° S to be covered. The sampling profile in 1978 was similar to that flown in 1977, consisting of a stair step configuration which alternated between boundary layer air and the free troposphere (see Fig. 1).

Operationally, the 1978 spring flight program was a major success. Scientifically, it is still early for any final verdict to be given, however, based just on the real time observations made during the flight (plus very limited post-flight analysis) major new findings again appear to be forthcoming from the 1978 program. In particular, further improvements made in the calibration techniques on several instruments appear to have resulted in both more extensive as well as higher caliber data than on the 1977 mission. In the text that follows, some preliminary summary statements have been provided as they relate to observations made on several key trace gases during the 1978 flight operation.

O_3

One of the major findings on ozone in 1977 was that of observing ozone layers in the middle and lower troposphere over thousands of miles of the South Pacific Ocean. However, a major question raised by those observations was: How common an event is ozone layering in the South Pacific? The 1978 spring flights have clearly shown that the mechanism by which ozone is transported from the stratosphere to low altitudes at low latitudes in the troposphere is one which operates a good fraction of the time. As in 1977, throughout remote tropical and sub-tropical areas of the

1978 SPRING GAMETAG FLIGHT OPERATION



Pacific, average ozone levels in the free troposphere were at least a factor of two higher than measured in the boundary layer. The latter observation was true for both the southern and northern hemispheres. However, during the 1978 flights, intense ozone layers were observed only in flights north of the ITC zone ($\sim 11^{\circ}$ N). One possible reason for this could have been the difference in longitude covered in the northern and southern hemispheric operations. In the northern hemisphere the longitude range was 120° W to 170° W. In the southern hemisphere the operating range was 170° W to 170° E.

A new finding on ozone in the tropical latitude range of $\sim 0^{\circ}$ to 10° S was an observed major drop in the ozone level in the marine boundary layer. Typical values were in the 2-6 ppb range. Some depression was also observed in the free tropospheric value of ozone (from 35-40 down to 20-25 ppb) over the same latitude range, but the percent decrease was considerably less than in the boundary layer.

Ozone levels when measured in remote areas at mid or high latitudes were either the same in both the boundary layer and free troposphere or were somewhat higher in the free troposphere. On at least three occasions when sampling at mid-latitudes, a major difference in the boundary layer versus free tropospheric value of ozone was observed when our sampling track took us through three well defined tropopause folds. These folds, involving three different flights, were all observed in the latitude range of 37° N to 45° N. During one of these penetrations, ozone levels approaching 200 ppb were observed. No tropopause folds were observed in the southern hemisphere during the 1978 sampling operation.

A final observation on ozone concerns the evidence found for the importance of photochemically produced ozone in the troposphere. As noted earlier in the text, in those areas sampled which were remote and unpopulated,

under no set of conditions was the ozone level in the marine or continental boundary layer ever found to be higher than that observed in the free troposphere. In most cases, however, when sampling occurred in moderately or highly populated areas having moderately high ground temperatures (i.e.> 26° C), boundary layer ozone values exceeded those observed in the free troposphere.

Although considerable detailed analyses of the ozone data from the 1977 and 1978 GAMETAG flights remains, several tentative conclusions seem appropriate at this time:

(1) Ground based ozone observations are wholely inadequate as a means of assessing the global tropospheric ozone budget.

(2) The tropospheric ozone budget in tropical and subtropical marine areas of the world has been significantly underestimated.

(3) Transport of ozone from the stratosphere at low, middle, and high latitudes appears to be by far the most important source of ozone in the troposphere. (Thus far only in populated continental areas under warm weather conditions is there any evidence of the importance of photochemically generated ozone.)

(4) It is possible that the gradient of ozone between the atmospheric boundary layer and the free troposphere may represent one of several important global environmental criteria which might be used to evaluate air quality in the lower atmosphere.

CO

In 1977 two different grab sampling techniques were employed during the GAMETAG flights. These two approaches resulted in significantly different answers for the northern-southern hemispheric gradient for CO, i.e. 1.3 versus 2. One of the objectives of the 1978 flight was to resolve this discrepancy by having on board the aircraft a real-time measuring CO instrument. During the 1978 GAMETAG operation, the instrument selected was an aircraft compatible gas-chromatograph. Preliminary analysis of data collected in the field, combined with grab samples which have been analyzed in the laboratory since the flight, now indicate that in the 1977 flight the low value determined for the interhemispheric CO gradient of 1.3 was in error. The problem identified is that of CO outgassing from the collection vessel upon being stored, awaiting laboratory analysis.

Preliminary analysis of 1978 data from the real-time measuring GC has shown an equatorial gradient for CO of $\sim$2.0 and a maximum inter-hemispheric CO gradient of $\sim$2.5. These data show only a minor gradient in CO from 0° to 57° S latitude (i.e. <15%). In the northern hemisphere, from 20° N to 70° N only a 20-25% gradient was observed with the maximum CO concentration occurring near $35\text{-}40^{\circ}$ N. Over remote areas sampled, very little gradient existed between boundary layer and free tropospheric samples.

The results reported above as well as those from 1977 are in considerable contrast to those reported by Seiler (1974). However, more recent measurements by Seiler (as yet unpublished) have resulted in interhemispheric CO data which are much closer in appearance to the 1977-1978 GAMETAG data. The maximum interhemispheric gradient resulting from the most recent Seiler data was $\sim$3.0. The possible reconciliation of Seiler's data with those of the 1977 and 1978 GAMETAG flights is now considered to be an important program objective during the non-sampling year (1979) of the GAMETAG Phase I program.

CH_3CCl_3

Preliminary results from the real-time GLC measurements taken during the 1978 flight program again point to a very small interhemispheric gradient for CH_3CCl_3. These measurements are therefore in good agreement with those recorded on the 1977 GAMETAG flight and are in contrast to those reported by other investigators in 1975 and 1976.

SO_2

Major improvements in the performance characteristics of the real-time measuring SO_2 analyzer resulted in a much more extensive set of SO_2 measurements in 1978. Very preliminary results in this case would indicate that in remote marine and continental areas sampled, the SO_2 level is normally less than 150 ppt. Three additional real-time observations which could be of major importance but must be verified in subsequent detailed analyses of the data are: (1) SO_2 levels in remote marine and continental areas are a factor of two to three times lower in the boundary layer than in the free troposphere. (This was not the case for sampling occurring over populated areas where boundary layer values in some cases actually exceeded the free tropospheric concentration value.) (2) Over the latitude range of 0° to 10° S a substantial drop occurred in the SO_2 concentration both in the boundary layer as well as the free troposphere. This is the same region where a major drop in the O_3 level was observed. And, (3) there appears to be a significant roll-off in the level of SO_2 at high latitudes both in the northern and southern hemispheres.

COS

Preliminary results on the levels of COS in both the northern and southern hemispheres indicate that very little if any gradient exists. A detailed analysis of the 1978 data will be necessary before any final conclusion can be drawn on this point. If this compound is primarily being released from anthropogenic sources (not yet established) and its lifetime is long, the possible impact of COS on stratospheric aerosol loading may have to be examined in far greater detail (Crutzen, 1976).

NO

During the 1977 GAMETAG flights, considerable difficulty was encountered in the operation of the NO chemiluminescent analyzer. One of the major problems discovered during that flight was that of an H_2O interference. This was most serious therefore when sampling boundary layer air in the South Pacific. Thus, only an upper limit of 150 ppt of NO could be assigned to clean air in the South Pacific. Several changes were made in the configuration of this instrument in preparation for the 1978 GAMETAG flights. During the 1978 operation, typical free tropospheric values of NO were measured to be ~40 pptv and boundary layer concentrations in the South Pacific were ~50 pptv. However, a carefully executed day-night flight in the middle of the South Pacific operation showed that a significant fraction of the signal (i.e. equivalent to ~30 pptv of NO) being measured as ambient NO was a chemical interference signal whose source could not be identified. Thus, at this time we believe that NO levels in the South Pacific are in the range of 20 pptv or less.

OH

Although no data has yet been processed from the 1978 flight, it is noteworthy that OH data was collected on all twenty GAMETAG flights.

The instrumentation operated throughout the duration of the 1973 program without any major problems developing.